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SOIL ACIDITY AND A FIELD METHOD FOR ITS MEASUREMENT[1]

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In a note on " Plant Distribution around Salt Marshes in Relation to Soil Acidity,"[2] the writer stated that many conclusions as to the relation between the distribution of plants and the reaction (acidity or alkalinity) of soils have been based on "misleading methods or unsound views as to the nature of soil acidity." It seems desirable that some evidence in support of this claim should be placed on record. The questions which have been most frequently asked the writer concerning the cause of soil acidity, the methods by which it can be measured, etc., will be answered as fully as possible from the standpoint of modern physical chemistry.[3]

WHAT IS THE CAUSE OF SOIL ACIDITY?

Soil acidity has been discussed by numerous workers, but considerable confusion as to its nature appears still to exist. To quote from a recent paper:[4] " Investigators have looked to the following substances and phenomena for the explanation of soil acidity: the presence of mineral acids, the presence of organic acids, free hydrogen ions, colloidal material, absorption and adsorption, and the presence of specific compounds." The writer of the foregoing added as his own view "hydrolytic mass action phenomena." Only one of the " substances and phenomena " of this list can be regarded as a direct " explanation of soil acidity," namely, the *presence of hydrogen-ion.*

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[1] [The influence of soil acidity on plant distribution has been amply demonstrated (Coville, U. S. Dep't. Agr. B. P. I., Bull. 193, 1910; Truog, Soil Science, 5: 169, 1918; 7: 469, 1919; Gillespie and Lewis, Soil Science, 4: 313, 1917; and many others). Its influence upon the animals living in the soil remains to be studied, but probably will prove no less important. Dr. Wherry discusses in simple terms the principles of physical chemistry which bear upon soil acidity, but usually can be found only in the more technical and less easily understood works. For convenience, his field method of measuring soil acidity (already published in the Jour. Wash. Acad. Sci. 10: 217, 1920) is included, and his indicator chart is reproduced for the first time in actual colors.—EDITOR.]

[2] Ecology, Vol. I, No. 1, pp. 42–48, 1920.

[3] It is a pleasure to acknowledge the aid received in the preparation of this paper from colleagues, especially from Dr. E. Q. Adams of the Bureau of Chemistry.

[4] Noyes, H. A., Journ. Ind. Eng. Chem., 11: 1040. 1919.

WHAT IS HYDROGEN-ION?

According to the almost universally accepted electrolytic-dissociation or ionization theory, many chemical compounds, under certain conditions, exhibit dissociation into electrically charged portions, known as *ions*. These may consist of single atoms or of groups of atoms. Only ionization connected with the dissolving of substances in water need concern us here. Compounds differ widely in the extent to which they are dissociated or ionized in dilute aqueous solution. Among inorganic compounds—acids, bases, and salts—many are almost completely, others only partially, ionized. Of organic compounds a few, especially acids, are markedly, a considerable number slightly, and many not appreciably ionized.

Water itself dissociates into *hydrogen-ion,* made up of positively charged hydrogen atoms, and accordingly symbolized by H^+; and *hydroxyl-ion,* made up of negatively charged hydroxyl (hydrogen plus oxygen) groups, symbolized by $(OH)^-$. Acids yield hydrogen-ion and another ion consisting of the balance of their constituents; thus from nitric acid, HNO_3, arise H^+ and $(NO_3)^-$, the latter being termed nitrate-ion. Alkalies yield hydroxyl-ion and another consisting of the remainder of the compounds; in potassium hydroxide, KOH, the ions are $(OH)^-$ and potassium-ion, K^+.

The amount of hydrogen-ion present in a solution, expressed as gram-equivalents per liter, is often referred to as the *hydrogen-ion concentration.*

The water existing in soils, as a film around the solid soil particles, does not differ essentially from free water in the above respects. Substances can dissolve in it, undergo ionization, and give rise to a definite hydrogen-ion concentration of the soil.

WHY SHOULD HYDROGEN-ION BE CONSIDERED IN CONNECTION WITH ACIDITY?

Observation has shown that the properties of substances which lead to their classification as acids are directly connected with the presence of hydrogen-ion in their solutions. The characteristic sour taste—from which the term acid was of course originally derived—is in considerable part the taste of hydrogen-ion.[5] Reddening of blue litmus, the most widely known test for acidity, is produced by hydrogen-ion. And it is hydrogen-ion which takes part in most of the chemical changes into which acids enter.

The inhibiting effect of acids on the growth of many bacteria, and the favorable effect they show toward the growth of some molds and fungi, are hydrogen-ion phenomena. There is every reason to suppose that the action of acids on higher organisms, such as the flowering plants, is identical in origin. It is evident from these considerations that the hydrogen-ion concentration is a highly important feature of the solution of any acid substance.

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[5] Harvey, R. B., Journ. Amer. Chem. Soc., 42: 712. 1920.

HOW DOES HYDROGEN-ION CONCENTRATION DIFFER FROM QUANTITY OF ACID?

The difference between these two factors in the case of two typical acids is here tabulated. The numerical values given are only approximate.

TABLE 1. *Difference between hydrogen-ion concentration and quantity of acid in normal solutions of two acids*

	Acid	
	Hydrochloric	Formic
Formula	HCl	$H(CHO_2)$
Molecular weight = equivalent weight = grams per liter in normal (molar) solution	36.5	46.0
Quantity of acidic hydrogen, grams per liter	1	1
Physico-chemical class	strong	moderately weak
Percent. to which ionized	75	1
Corresponding hydrogen-ion concentration, grams per liter	0.75	0.01
Specific acidity	7,500,000	100,000

Table 1 shows that although a normal (molar) solution of both acids contains the same quantity of acidic hydrogen, the strong acid yields 75 times as much hydrogen-ion as does the moderately weak one, and may be expected to have 75 times as much effect in the directions listed under the preceding heading.

The situation is analogous to that of two men, both possessing $100, but one having $25 in a savings bank and $75 in his pocket, the other having $99 and $1 in these respective places. The first man can purchase 75 times the amount of any commodity that the second can, even though the total quantity of money they own is the same. Purchasing power, in this illustration, corresponds exactly to hydrogen-ion concentration; for the amount of hydrogen which is ionized, not the total amount, determines most of the things an acid can do.

HOW MAY HYDROGEN-ION CONCENTRATION BE MOST SATISFACTORILY EXPRESSED?

The relations between the various methods of expressing hydrogen-ion concentration which have been proposed can best be indicated by a tabular arrangement. In Table 2 the way two values selected at random appear under all of them is brought out; and the reader may judge whether the one chosen for use in the present paper (the last one tabulated, specific acidity) is not the best from the point of view of clearness and convenience. The hydrogen-ion concentrations of the two solutions, in gram-equivalents per liter, are 0.0004 and 0.0000002 respectively, the former representing 2,000 times as much hydrogen-ion as the latter.

TABLE 2. *Comparison of methods of stating hydrogen-ion concentration*[6]

	Method	Solution 1	Solution 2
Concentration	Actual number	0.0004	0.0000002
	Power of 10 with a coefficient.....	0.4×10^{-3}	0.2×10^{-6}
	Power of 10	$10^{-3.4}$	$10^{-6.7}$
Potential due to $H^+(P_H)$		3.4	6.7
Chemical potential, X_H	exponent	3.6	0.3
	power of 10	$10^{3.6}$	$10^{0.3}$
Specific acidity (water as unit)		4000	2

TABLE 3. *Specific acidity and alkalinity equivalents of P_H values*

A. Integral values of P_H

P_H	X_H	Specific acidity	P_H	X_H	Specific alkalinity
0	7	10,000,000	7	0	1
1	6	1,000,000	8	−1	10
2	5	100,000	9	−2	100
3	4	10,000	10	−3	1,000
4	3	1,000	11	−4	10,000
5	2	100	12	−5	100,000
6	1	10	13	−6	1,000,000
7	0	1	14	−7	10,000,000

B. Decimals of P_H

P_H	X_H	Specific acidity	P_H	X_H	Specific alkalinity
6.0	1.0	10 (10.00)	7.0	0.0	1 (1.00)
6.1	0.9	8 (7.94)	7.1	−0.1	1.3 (1.26)
6.2	0.8	6 (6.31)	7.2	−0.2	1.5 (1.58)
6.3	0.7	5 (5.01)	7.3	−0.3	2 (2.00)
6.4	0.6	4 (3.98)	7.4	−0.4	2.5 (2.51)
6.5	0.5	3 (3.16)	7.5	−0.5	3 (3.16)
6.6	0.4	2.5 (2.51)	7.6	−0.6	4 (3.98)
6.7	0.3	2 (2.00)	7.7	−0.7	5 (5.01)
6.8	0.2	1.5 (1.58)	7.8	−0.8	6 (6.31)
6.9	0.1	1.3 (1.26)	7.9	−0.9	8 (7.94)
7.0	0.0	1 (1.00)	8.0	−1.0	10 (10.00)
(For each lower P_H unit, multiply the specific acidity by 10)			(For each higher P_H unit, multiply the specific alkalinity by 10)		

The method illustrated in the last line of Table 2 obviously shows with a minimum of calculation on the part of the reader that one of the solutions is

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[6] The last two methods have been explained by the writer, Journ. Wash. Acad. Sci., 9:305. 1919.

2,000 times as acid as the other; and it gives directly the information that the hydrogen-ion concentration is in the one case 4,000 times, in the other case twice, that of pure water.

As the P_H method is rather widely used in the statement of hydrogen-ion concentration, it seems desirable that another table be given showing the relations between P_H values and specific acidities (and alkalinities) over the range covered by dilute aqueous solutions.

WHAT SUBSTANCES MAY YIELD HYDROGEN-ION TO THE SOIL SOLUTION?

This question can also be most instructively answered by a tabular statement.

TABLE 4. *Soil constituents yielding hydrogen-ion*

1. *Directly* (*when treated with water alone*)

A. Inorganic.
  a. Strong, highly ionized acids, like hydrochloric, sulfuric, etc.
  b. Weak, slightly ionized acids, especially carbonic.
  c. Acid salts, like potassium acid sulfate, which may be moderately or slightly ionized (as acids).
  d. Salts of weak bases with strong acids, like aluminium chloride, ammonium sulfate, etc., which are slightly hydrolyzed and therefore yield a small amount of hydrogen-ion.
B. Organic.
  a. Strong, highly ionized acids, like oxalic.
  b. Weak, slightly ionized acids, like acetic.
  c. Acid salts, like potassium acid sulfate, which may be moderately or slightly ionized (as acids).
  d. Salts of weak bases with strong acids, like aluminium citrate, ammonium oxalate, etc., which are hydrolyzed as in *A. d.*
  e. Amino-acids, like aspartic (aminosuccinic) acid, which are internal salts in the sense that the acidity is neutralized by the amino group, and which may be moderately or slightly ionized.
  f. Humic acids, which if they exist at all are slightly ionized.

2. *Indirectly* (*when treated with solutions of salts*)

A. Inorganic, especially colloidal clay.
B. Organic, especially colloidal humus.

From the above tabulation it is evident that soil acidity is likely to be a rather complex phenomenon, and it is certainly misleading for an investigator to look to any single substance or type of substances as the source of the hydrogen-ion producing it in all cases. As it seems probable, however, that comparatively few of these possible sources of hydrogen-ion, and accordingly of acidity, coexist in appreciable amounts in any one soil, the evidence for the presence of the several types of acid substances may well be reviewed.

ARE INORGANIC ACIDS PRESENT IN NATURAL SOILS?

There appears to be no reason to doubt that strong, highly ionized, inorganic acids exist in appreciable quantities in some soils. Nitric acid may be produced by nitrifying bacteria, sulfuric acid by the oxidation of sulfur-bearing compounds, hydrochloric acid through the interaction of sea-water and soils in the vicinity of salt marshes. Certain muck soils have been observed by Plummer[7] to exhibit hydrogen-ion concentrations equivalent to specific acidities as high as 200,000, which are comparable with the values shown by hundredth normal solutions of these acids.

The weak, slightly ionized carbonic acid, H_2CO_3, is probably universally present in soils, where it arises from the decomposition of carbonaceous matter. It can yield a maximum specific acidity of over 500, although in the presence of bicarbonate ion, which is rarely absent from the soil solution, this value may be greatly lessened.

If strong dibasic acids such as sulfuric develop in soils, and attackable compounds of potassium or other univalent elements are present in amounts insufficient to neutralize the acid completely, then acid salts will be formed. Potassium acid sulfate, $HKSO_4$, is rather highly ionized in dilute solution, yielding some hydrogen-ion (as well as various other ions), so this is by no means an unlikely source of soil acidity in certain cases.

Salts of aluminium and of iron may readily be formed by the action of strong acids upon silicates containing these elements; and such salts, because of the weakness of the bases, will through hydrolysis yield more or less hydrogen-ion. Similar relations hold for salts of ammonia and its derivatives, produced by the decomposition of nitrogenous organic matter; the bases are weak, and the salts yield hydrogen-ion. Such salts of weak bases with strong acids are likely to be the source of a considerable portion of the acidity of certain soils.

ARE ORGANIC ACIDS PRESENT IN SOILS?

Cellulose and other constituents of plant tissues are continually becoming incorporated with the soil. These decompose under the influence of various microorganisms, and among the decomposition products organic acids are likely to be represented. These may include strong, highly ionized acids like oxalic; moderately ionized ones like lactic; and weak, slightly ionized ones like acetic. Acid salts of any of these acids which are polybasic may form, as with inorganic acids; and the stronger of the organic acids may unite with weak bases to form salts, the result in both cases being the liberation of hydrogen-ion. Amino-acids are likely to develop from the decomposition of nitrogenous plant constituents, and also yield their quota of hydrogen-ion.

[7] Journ. Agr. Research, 12: 22. 1918.

Probably no subject connected with soil acidity has been so extensively discussed as the question whether humic acids and related substances exist or not. It is not the intention of the writer to take sides in this controversy, but the physical-chemical aspect of the question may be briefly stated. It appears to have been definitely established that humus contains one or more substances which yield hydrogen-ion to pure water, and are therefore to be classed as acidic. Whether these substances are (1) of definite composition, and have their acidic hydrogen present in stoichiometric proportions; or (2), indefinite in composition, colloidal in character, and containing variable amounts of adsorbed hydrogen-ion, appears to be the chief point in dispute. Such sound evidence as has been presented seems to the writer to favor the second view, but as the matter has not been entirely settled, it is best to leave in the table a place for humic acids as a partial cause of soil acidity.

What is a Colloid?

The term *colloid,* which is used (as an adjective) in the preceding paragraph, as well as in the final subdivision of Table 4, can be defined in a variety of ways, depending upon the use to which the definition is to be put. For the purposes of the present study, a colloid is any substance of which the constituent particles are of such size and shape that adsorption phenomena are prominently exhibited. *Adsorption* means the sticking of atoms, ions, or molecules of one substance to the surfaces of the particles of another substance. Nothing would be gained by entering into a discussion as to whether this effect is physical or chemical in nature, for there is good reason to believe it to represent a combination of both. It is physical in that adhesion and electromagnetic forces play a part in joining the substances. It is chemical in the sense that there is a union between the atoms of the substances by means of valence bonds, although since only atoms lying at the surfaces of the particles of the adsorbing substance take part, stoichiometric relations are not recognizable. The degree to which adsorption occurs in any given case depends, then, on the size and shape of the particles concerned, as well as on their chemical nature.

Soils contain colloids of two kinds, inorganic and organic. The former includes finely divided quartz and other minerals, silica gel, and gel forms of various more or less definite aluminium silicates, by far the most frequent of which has the formula $Al_2O_3.2SiO_2$. These substances are usually collectively known as clay. The organic colloids, conveniently grouped together under the term humus, comprise various complex compounds of carbon, hydrogen, and oxygen, arising from the partial distintegration of cellulose.

WHAT IS THE SIGNIFICANCE OF SUBSTANCES YIELDING HYDROGEN-ION INDIRECTLY?

Only the hydrogen-ion developed directly by water in the soil can have any influence on the growth of plants; for the latter have no clairvoyant powers, and can not respond in any way to acidity which does not exist, but which the soil has merely the ability to produce when treated with certain chemical substances. Since, however, writers on soil acidity often overlook this fact, and discuss indirectly-produced acidity as if it affected plants, and since many of the methods proposed for determining "lime-requirement" are based on the measurement of this type of acidity, the indirect production of acidity will be discussed in outline here.

When a solution of a neutral salt, like calcium chloride, is added to a soil, the solution becomes more or less strongly acid. This is not the result of a single process, but is the combined effect of several, including the following:

Double Decomposition.—Aluminium silicate plus calcium chloride yields calcium silicate plus aluminium chloride; the last, being a salt of strong acid with a weak base, yields hydrogen-ion, and hence an acid reaction, to the solution.

Replacement of Ions.—Calcium ion from the solution may replace aluminium ion present in an adsorbed form on the surfaces of the particles of the soil colloids, the net result being essentially the same as in the preceding paragraph. Calcium ion may also replace hydrogen-ion adsorbed on the colloids, whereupon the solution will become acid; this is quantitatively by far the most important source of indirect acidity.

Coagulation of Colloids.—Calcium chloride and other salts have the power of coagulating colloids, and reducing correspondingly their power of adsorption; acidity may be produced by the ions thus set free just as in preceding instances.

The first of these processes is to be expected only with the clayey matter in the soil, but the other two apply to both clay and humus. The more colloidal material a soil contains the greater is likely to be the acidifying effect of adding a neutral salt.

HOW CAN THE CAUSE OF SOIL ACIDITY BE RECOGNIZED IN A GIVEN CASE?

The acidity of a soil may be due to the simultaneous presence of so many different substances that no general procedure for the identification of individual ones can be formulated. The following plan, however, permits of the recognition of whether the principal acid present is highly, moderately, or only slightly, ionized.

Stir up about 25 grams of soil with 50 c.c. of distilled water, allow to settle, and decant the liquid upon a small filter paper, throwing away the first few c.c. coming through (since they contain traces of acid extracted from the paper). Test the acidity of the filtrate by placing 1 cc. of it in a test tube and adding a drop of methyl red indicator; if its least acid color, yellow, is shown, repeat with brom-cresol purple indicator. Prepare a solution of hydrochloric acid of such dilution that 1 c.c. of it gives with the same indicator a color exactly matching that produced by the soil extract. Then prepare a solution of sodium hydroxide about 10 times as strong, on the molar basis, as is the acid.

Into two similar beakers place 10 cc. each of the soil extract and the acid solution, and add an indicator which shows its color changes at the physico-chemical neutral point, such as litmus or the more brilliant brom-thymol blue. Titrate both solutions with the sodium hydroxide solution. If both require approximately the same quantity of this alkali, the acidity of the soil is chiefly due to the presence of an acid comparable in strength—that is, in degree of ionization—to hydrochloric acid. If twice as much alkali is required for the soil extract as for the hydrochloric acid solution, then the acidity is chiefly due to a moderately strong acid, such as, for instance, lactic acid. If several times as much alkali is required for the soil extract as for the hydrochloric acid solution, then a weak acid is concerned in the production of the soil acidity.

The writer has tried this method with several acid soils, and has found the results to indicate the presence of moderately strong acid substances.

How Can Soil Acidity be Measured?

In order to have a basis for discussion, it will be desirable to tabulate the methods which have been suggested, in more or less chronological sequence, bringing together related ones.

TABLE 5. *Methods of measuring acidity present and producible in soils*

1. A salt solution is added to the soil; for this purpose there have been used: sodium chloride, potassium chloride and nitrate, calcium chloride, nitrate and acetate, zinc sulfide plus calcium chloride, etc. The quantity of acid in the resulting solution, which represents that originally present in the soil plus a much greater amount produced indirectly by the processes outlined on a previous page, is then determined by titration or other means.
2. No salt solution, but some pure water, is added to the soil.
   - *A*. The mixture is titrated with lime water, using either an indicator, or observation of the freezing point, to determine the end point. This gives the amount of lime needed to neutralize the acid originally present in the soil plus that produced indirectly by the action of lime (which is likely to differ from that produced by a neutral salt solution) as well as the amount of lime required to satisfy the adsorptive power of the soil colloids for calcium ion under the given conditions.
   - *B*. The mixture is filtered, and the filtrate titrated with standard alkali. This gives the quantity of acid present in the soil.
   - *C*. The hydrogen-ion concentration or specific acidity is determined:
     - *a*. By catalysis of an ester.

b. By measurement of the potential due to hydrogen-ion with the potentiometer.
c. By observation of color changes of indicators whose relations to hydrogen-ion concentration are known.

From the discussion of the indirect production of acidity in soils already given it is evident that the methods listed under 1 in Table 5 are *not* methods of determining the acidity originally present in a soil. The results they yield are composite, representing both acid originally present and a usually greater quantity produced by the treatment. That the results obtained would differ widely with the salt used and with the conditions of the experiment would naturally be expected, and has been demonstrated by actual trial.[8] Even when soils are neutral or alkaline at the start they may develop a considerable acidity when treated with a salt solution; and any method which indicates an alkaline soil to be acid is certainly valueless for the determination of the effect of acidity on plant growth.

By way of analogy, suppose a man has one pocket full of coins, and another full of slugs. In so far as his ability to purchase commodities is naturally be expected, and has been demonstrated by actual trial.[8] Even though the slugs can, by appropriate procedure, be converted into coins, they have only potential and no direct purchasing power. Determination of the total number of metal objects, or of the total weight of metal, which the man carries, can of course be carried out with as high a degree of precision as desired; but what bearing will this data have on his actual wealth?

While some writers erroneously regard these methods as yielding values for soil acidity, others merely claim them to be "lime-requirement" methods, this term being understood to refer to the amount of lime which must be added to the soil per acre-foot (or other unit of area and of depth) to render its reaction neutral. The amount of lime needed to neutralize the acidity of a solution produced by the action of an arbitrarily selected salt upon a soil is, however, not necessarily related in any way to the amount of lime which would be needed to neutralize the soil when applied directly (as described under *2 A*, in Table 5). It is therefore also erroneous to term these methods lime-requirement methods.

Since the methods in this group yield composite, variable, and contradictory results, and furnish no information as to the soil acidity nor as to the lime-requirement, it can only be concluded that they are valueless in connection with any study of soils in relation to plant growth.

The writer is impelled to make these strong statements because of the appalling amount of time and energy which is being expended in applying these salt-solution acidification methods. Articles are continually being published, in which important conclusions as to relations between soils and plants are based on results obtained by them; and commercial organizations are putting on the market apparatus for carrying them out. It is hoped that the present paper will at least lead future workers to reflect upon the significance of any proposed method of studying soils, before deciding to adopt it.

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[8] Ames and Schollenberger, Journ. Ind. Eng. Chem., **8**: 243. 1916; under some conditions different salts may yield, however, approximately the same result: Knight, Journ. Ind. Eng. Chem., **12**: 340. 1920.

Taking up now the methods listed under 2 *A,* in Table 5, it may be stated that the lime-water (Veitch) method gives directly the amount of lime needed to bring the soil to the degree of acidity or alkalinity shown by the indicator used. If phenolphthalein is selected, the result is the amount of lime which will give the soil a specific alkalinity of 30. If, however, litmus or brom-thymol blue were to be used, the amount of lime required to render the soil neutral would be obtained. This method, then, though obviously not permitting the determination of soil acidity, is *a real lime-requirement method.* If the freezing point of the soil solution is used to indicate the course of the titration, it may be possible to recognize individually the point at which acid is neutralized as well as that at which lime ceases to be taken up by the soil; so that this method is capable of yielding both quantity of acid and lime-requirement.

The method given under 2 *B,* in Table 5, permits the determination of the *quantity* of acid present in a given soil in the simplest possible way. An indicator whose color changes occur at the neutral point should, however, be used. Neither methyl orange nor phenolphthalein, however useful they may be for obtaining comparative results in ordinary titrations, shows when a solution has been actually neutralized. When an acid solution is being titrated, the former changes its color long before the neutral point has been reached and the latter does not begin to change until well past neutrality.

For reasons already explained in detail, the quantity of acid present in a soil is far less significant than the hydrogen-ion concentration or specific acidity, when effect upon the growth of plants is under consideration. The methods under 2 *C,* in Table 5, are therefore the only ones which should be used in studying this subject. Method *a* is difficult to apply and to interpret. Method *b* is justly resorted to for testing soils where the necessary apparatus is available. A portable apparatus, suitable for determining the electrical potential of soil solutions in the field has recently been designed by Professor S. F. Acree and collaborators,[9] and should prove very useful for work of this sort.

FIELD METHOD OF MEASURING SOIL ACIDITY

The indicator method, *c,*[10] while less accurate than the potentiometer method is, however, so simple to apply that it can be recommended for use in all ordinary studies of soil acidity in relation to plant growth.[11] Under the most favorable conditions it is possible by the indicator method to measure acidity and alkalinity with much greater precision than is necessary in the field. By treating the indicators with buffer solutions of known ionic concentration, many hues intermediate between those in the accompanying color chart can be distinguished. On comparing the colors thus produced with those developed by mixing clarified soil extracts with the same indicators, specific acidities differing by a factor of $\sqrt[5]{10}$ or 1.59 ($P_H = 0.2$) can be recognized. In the field, where it is inconvenient to carry buffer solutions to prepare standards for comparison, and where the turbidity of soil extracts is difficult to remove, it is impracticable to work closer than values differing by a factor of $\sqrt{10}$ or 3.16 ($P_H = 0.5$) which is rounded off for simplicity to 3+. This degree of precision is, however, entirely adequate for the purpose in view, for it has been repeatedly found that from one to another plant of the same species, or indeed, from one to another root on the same individual, separate observations of reaction may differ by a factor of 10 or more.

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[9] For sale by the Will Corporation, Rochester, New York.

[10] Clark and Lubs, Jour. Bacteriology, 2: 1, 1917; Gillespie, Jour. Wash. Acad. Sci., 6: 7, 1916.

The following outfit is used.[12] First, a rectangular box about 3.5 × 5 × 9 cm. in dimensions. In the box, six vials for the indicators, 1.5 × 5.5 cm., capacity 8 c.c., each provided with a cork or rubber stopper, into which is inserted a glass rod flush with the top of the stopper, and extending nearly to the bottom of the vial; to prevent undue compression upon inserting the stoppers, a groove may be cut in the side of each, so as to reach nearly to the lip of the vial. Then, three or four vials in which to extract the soils, about 2 × 5 cm., made of heavy glass, to prevent undue breakage; a container for water, which may conveniently be a screw-capped jar holding 200 c.c. or more, or an aluminum canteen; and a pipette, most simply constructed of two pieces of glass tubing a few cm. in length, connected by a rubber tube.

The six indicators which have proved most satisfactory in work with soils are: bromphenol blue, bromcresol purple, bromthymol blue, phenol red, methyl red, and *o*-cresolphthalein or phenolphthalein. The first three are used, as recommended by Clark and Lubs,[13] in about 1 percent solution in water, titrated with dilute sodium hydroxide to their intermediate colors; and the phenol red in a 0.5 percent solution similarly titrated. The methyl red and phenolphthalein are used as 0.05 percent solutions in 50 percent alcohol. It should be noted here that litmus paper, which is often recommended for testing soil reaction, is much less sensitive than the above indicators, and may give misleading results.[14]

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[11] The following description is reproduced, with minor modifications, from the Jour. Wash. Acad. Sci., 10: 217, 1920.

[12] Sets of indicators similar to that here described are for sale by the La Motte Chemical Products Co., 13 W. Saratoga St., Baltimore, Md.

[13] Journ. Bacteriology, 2: 135. 1917.

A simplification of the procedure previously recommended has been adopted; modifications may still be desirable in special cases. But before giving the directions, a word should be added concerning the water used for mixing with the soil. If calcium bicarbonate is present in this water, the soil acidity will be diminished; while if neutral salts, such as sodium chloride, and especially calcium sulfate, are present in any considerable amount, the acidity will be appreciably increased. The former effect is a direct neutralization; but the latter is due to the fact that the clay and the humus[15] in the soil adsorb the basic elements from neutral salts, and set the acid free. In the laboratory, distilled water can be used, and, to attain the greatest precision, air freed from carbon dioxide can be blown through it until it reacts quite neutral; when one is traveling, distilled water can usually be purchased from a drug store, and will give satisfactory results without special purification. In the wilds the best that can be done is to obtain spring or well water rising through rocks as free as possible from soluble constituents—such rocks as sandstone, shale or schist. In calcareous regions it may be necessary to test waters from one source after another until a sample is found which reacts neutral—is colored green by a drop of bromthymol blue indicator—and to arrange the trip so that the water supply can from time to time be replenished from this source.

With these points in mind, the following approximate directions have been drawn up:

A sample of soil a gram or two in weight is shaken from living roots into an empty vial, and 5 c.c. of the most nearly neutral and salt-free water available is added, the vial being shaken well to insure complete mixing. After the soil and water are thoroughly mixed, the solid matter may be compacted with a glass rod or a stick, and the vial then supported at an angle of 45° and allowed to stand until the bulk of the suspended matter has settled. The more or less clear liquid is then decanted or pipetted off into another vial, a drop or two of bromthymol blue or one of the other indicators, the color changes of which occur near the neutral portion of the table, are added, and the color assumed is noted. If either of the extreme colors is shown, the process is repeated with the indicator whose color changes come next in the corresponding direction; and this is continued until either an intermediate color of one indicator, or opposing extremes of two overlapping ones, are obtained, whereupon the specific acidity or alkalinity can be read off from the chart.

The more turbid the liquid, the more indicator must be added, and the less certain are the results obtained. The turbidity can, of course, be re-

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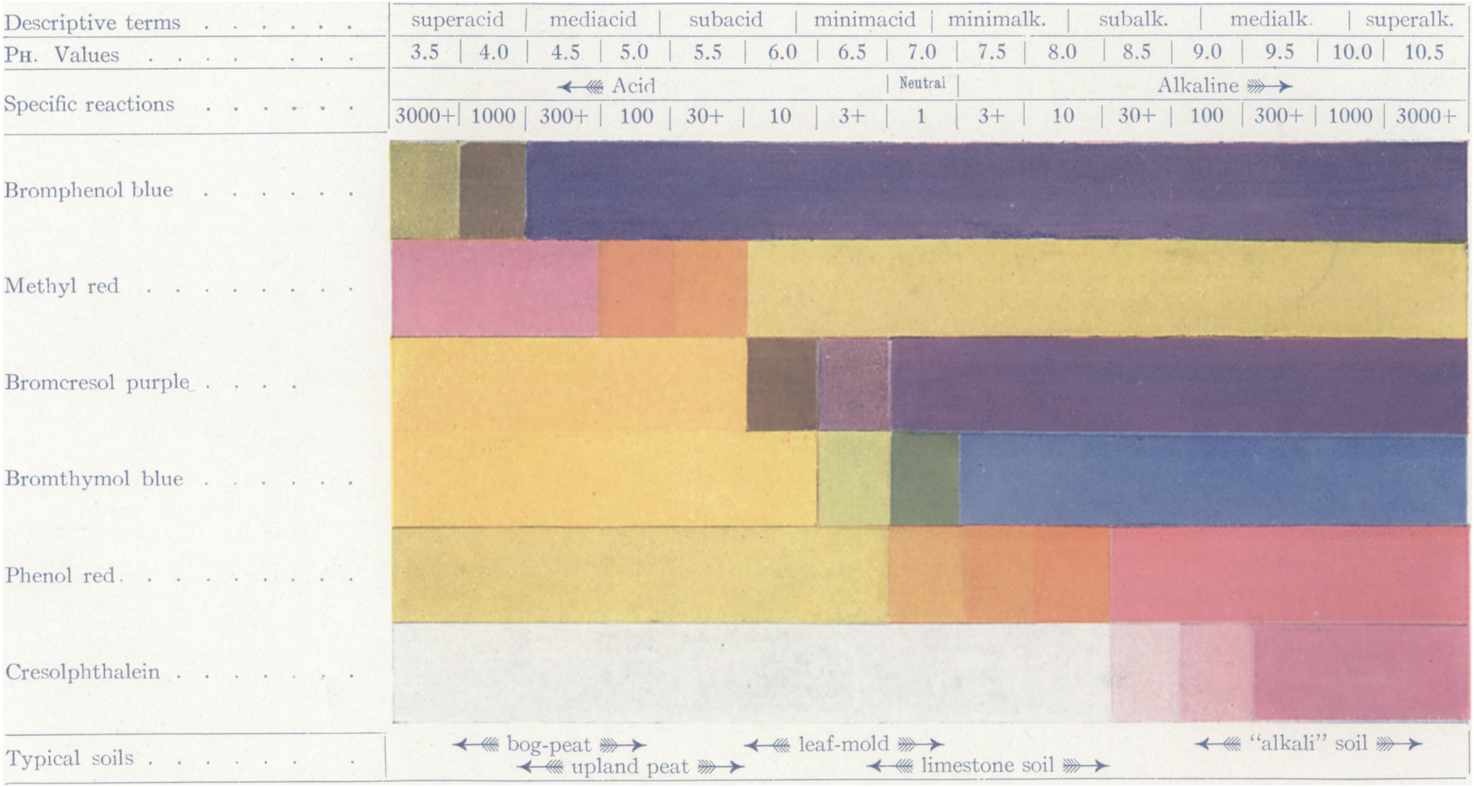
[14] Gillespie and Wise, Journn. Amer. Chem. Soc., 40: 796. 1918.

[15] Gillespie and Wise, op. cit.

CHART SHOWING COLORS OF INDICATORS USED FOR DETERMINING SOIL REACTIONS.



PH. Values	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5
Descriptive terms	superacid		mediacid		subacid		minimacid		minimalk.		subalk.		medialk.		superalk.
Specific reactions			←⋘ Acid					Neutral				Alkaline ⋙→			
	3000+	1000	300+	100	30+	10	3+	1	3+	10	30+	100	300+	1000	3000+
Bromphenol blue	🟨	🟫	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
Methyl red	🟥	🟥	🟥	🟧	🟧	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
Bromcresol purple	🟨	🟨	🟨	🟨	🟨	🟫	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
Bromthymol blue	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟩	🟦	🟦	🟦	🟦	🟦	🟦	🟦
Phenol red	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟧	🟧	🟧	🟥	🟥	🟥	🟥	🟥
Cresolphthalein	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	🟥	🟥	🟥	🟥	🟥

Typical soils

←⋘ bog-peat ⋙→
←⋘ upland peat ⋙→
←⋘ leaf-mold ⋙→
←⋘ limestone soil ⋙→
←⋘ "alkali" soil ⋙→

DIRECTIONS: To determine the specific acidity or alkalinity of a soil extract with the aid of this table, add first a drop bromthymol blue. If the liquid is colored green, the reaction is neutral; if yellow, it is acid; if blue, alkaline. If acid, repeat with successive indicators lying above bromthymol blue; if alkaline with those lying below. Continue until either an intermediate color of one of these indicators, or opposing extremes of two overlapping ones, are obtained. The specific acidity or alkalinity can then be found at the head or the corresponding column.

moved by the addition of coagulating agents or by filtration through paper; but it is essential to make certain that these do not in themselves show an acid or an alkaline reaction. The most satisfactory results of all can be obtained by running a quantity of the soil through a paper filter until two successive portions yield the same value when tested with indicators. But such procedures are more suited to laboratory than to field studies, and after a little experience one can tell the indicator color-change with certainty, even in the presence of considerable brown mud.

To illustrate the procedure followed in actual practice, two typical cases encountered by the writer may be cited here.

1. A black soil in pockets in limestone rock, supporting spleenwort ferns, was treated as above, and on testing the soil extract with bromthymol blue indicator, a strong blue color was obtained; reference to the chart showed that the reaction must be alkaline, and the value of specific alkalinity 3 or more ($P_H = 7.5$). The process was repeated with the indicator, the color changes of which lay next toward the alkaline side of the table, namely, phenol red. With this indicator a clear red color was obtained, showing the reaction to be actually specific alkalinity 10 ($P_H = 8.0$).

2. Soil from a dry blueberry thicket was tested, and, since upland peat is usually distinctly acid, the first indicator tried was bromcresol purple, the color changes of which occur just to the acid side of the neutral point; with this indicator a yellow color was obtained, indicating a specific acidity of at least 30. The soil was accordingly tried again with methyl red, which lies next toward the acid side, and this gave a violet-red color, corresponding to a specific acidity of 300 or more. It was accordingly necessary to try an indicator working at still higher acidities, namely bromphenol blue; and this yielded a violet color, indicating 300 or less. The last two indicators agreed, then, in fixing the reaction of this soil as: specific acidity 300 ($P_H = 4.5$).

In spite of certain limitations, this method is capable of giving definite information as to soil reaction in many cases. And the results obtained by the writer on a number of species of native plants, described in other communications,[16] have been of such significance that the method is published for the benefit of students of plant distribution and others interested in soil acidity and alkalinity.

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[16] Ecology, Vol. I, No. 1, pp. 42–48, 1920; Rhodora, **22**: 33, 1920; Am. Fern. Jour. 10: 15 and 46, 1920; Proc. Acad. Nat. Sci., Philadelphia, **1920**: 84 and 113.